



Visible light photocatalysis of dye-sensitized TiO₂: The selective aerobic oxidation of amines to imines

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ABSTRACT

Herein, we report an efficient protocol for the selective oxidation of amines with the sole involvement of conduction band electrons (e_{cb}^-) of TiO₂ for both the activation of O₂ and the ensuing oxidation reaction. Visible light was harvested by dye molecules on the surface of TiO₂, which injects electrons into its conduction band, generating dye radical cations. Charge transfers from dye radical cations to amines are relayed by the catalytic cycle of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) to TEMPO⁺, which is an oxidant that can conduct the direct two-electron oxidation of amines to imines. TEMPO was regenerated by the oxidation of TEMPOH with superoxide generated by the interaction of e_{cb}^- and O₂. This work suggests that one can exploit the strategy of cooperative photocatalysis with each component performing in its optimal role: TiO₂ for O₂ activation, dye for visible light harvesting, and TEMPO for oxidative transformations.

1. Introduction

TiO₂, consisting of two earth-abundant elements, is widely used in everyday life and has many potential applications that depend on its excellent properties [1,2]. It is under intensive investigation, with interest increasing greatly in recent years, resulting from it possibly offering an alternative capable of meeting energy and environmental challenges. The photoelectrochemically splitting of water on TiO₂ electrodes was discovered decades ago [3], and the photocatalytic events stemming from the interaction of light with the surface of TiO₂ have attracted great scientific attention ever since [4,5]. More importantly, it is endowed with one of the best photocatalytic activities of all metal oxides. However, TiO₂ can only be excited by UV light due to its inherent lack of visible light ($\lambda > 400$ nm) absorption [6–10].

Visible light, which can be provided by sunlight, is a secure and renewable source of energy that could be an ideal solution to many issues related to chemical transformations [11–14]. Visible-light-induced organic transformations are an appealing prospect that could realize the dual purposes of using renewable energy and reducing negative environmental consequences of chemical processes. However, these reactions are difficult to accomplish in practice [15,16]. Even though most organic chemicals that are encountered daily are ultimately dependent on natural photosynthesis, a visible-light-induced process. Thermally induced chemical transformations are still in the mainstream in both laboratory and industrial settings, in part due to the

difficulty in controlling the selectivity of photocatalytic oxidative transformations based on TiO₂. Because its oxidation potential of valence band hole (h_{vb}^+) is very high, leading to the generation of a variety of reactive oxygen species (ROS) [17].

To overcome these challenges, we implement a selective oxidation process without the involvement of h_{vb}^+ , resulting in the shutdown of the pathway for the generation of ROS from h_{vb}^+ . Meanwhile, the e_{cb}^- of TiO₂ activates O₂ to carry out further selective oxidation processes. One can employ a strategy of cooperative photocatalysis to explore the best of many worlds to achieve a smooth oxidation process [18]. In addition, nature's lead could be an inspiration for us to design efficient and selective catalytic oxidation systems. To this end, we want to design a metalloenzyme-like catalytic system [19] that can oxidize amines to imines under environmentally friendly conditions. This serves as a very convenient lead for our design. Specifically, a transition metal such as Cu and an organic co-factor such as quinone are important components of biomimetic catalysts to selectively oxidize amines [20].

Gaining inspiration from the metalloenzyme catalysis and our previous success in the photocatalytic selective aerobic oxidation of sulfides [21], herein we report the visible-light-induced selective oxidation of amines to imines with O₂ guided by the strategy of cooperative photocatalysis. The cooperation of a transition metal, Ti in TiO₂, and a co-factor, such as anthraquinone, can activate O₂ in a fashion resembling enzyme catalysis. In this case, an anthraquinone dye, alizarin red S (ARS), can harvest visible light to begin the photochemical reaction.

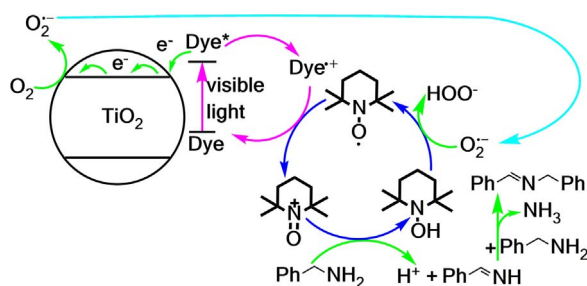
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Scheme 1. Proposed mechanism for the photocatalytic oxidation of amine to imine with O_2 by dye-sensitized TiO_2 and TEMPO under visible light irradiation.

The proposed mechanism for the cooperative photocatalytic oxidation of amines to imines with O_2 by dye-sensitized TiO_2 and TEMPO under visible light irradiation is shown in Scheme 1. ARS radical cations were formed after the injection of electrons into the conduction band of TiO_2 . If the oxidation of amines was directly initiated by ARS radical cations, the selectivity of imines would be difficult to control due to radical chain side reactions.

A suitable redox mediator was added to relay the electron transfer to ensure higher selectivity. The oxidation of amines requires two-electron oxidants to furnish imine products. $TEMPO^+$ is a two-electron oxidant that can conduct this selective two-electron oxidation of amines to imines, forming TEMPOH in the meantime [22]. ROS such as superoxide ($O_2^{\cdot-}$) can also be generated at the conduction band, which is used for the oxidation of TEMPOH to TEMPO. After these steps, the catalytic cycles and the final formation of product will be finished via this strategy of cooperative photocatalysis. This system not only takes advantage of each component's individual optimal functionality but also combines different factors to deliver the best results.

2. Experimental section

2.1. Reagents and solvents

All the reagents were obtained from commercial suppliers such as Sigma-Aldrich, Alfa Aesar and TCI, J & K Scientific, etc. The solvents were supplied by Merck, Fischer Scientific and Sinopharm Chemical Reagent Co., LTD. Benzyl- α,α - d_2 -amine was supplied by CDN Isotopes, Quebec, Canada. Anatase TiO_2 (Ishihara ST-01) used in this paper was purchased from Ishihara Sangyo Kaisha, LTD., Japan. ZnO , SiO_2 and γ - Al_2O_3 were purchased from XFNANO, Sigma-Aldrich and Aladdin respectively. All the reagents and solvents were directly used without further purification.

2.2. Procedure for the preparation of alizarin red S-sensitized TiO_2 (ARS- TiO_2)

The procedure for the preparation of ARS- TiO_2 is according to our previous report with slight modifications [21]. In detail, 0.6 mmol of ARS was put into a 100 mL beaker containing 40 mL of anhydrous ethanol for 10 min of ultrasonication. ARS is only slightly soluble in ethanol. But ultrasonication could disperse it uniformly. Then, 3 g of anatase TiO_2 (Ishihara ST-01) was put into the dispersed ARS in anhydrous ethanol for a further 10 min of ultrasonication. After that the mixture was magnetically stirred at 500 rpm for 12 h. Then ARS- TiO_2 was collected with a rotary evaporator equipped with a vacuum pump and subsequently dried at 100 °C at a vacuum drying chamber.

2.3. General procedure for the photocatalytic selective oxidation of amine

In a typical reaction, 10.7 mg of ARS- TiO_2 , 0.3 mmol of primary amines and 0.009 mmol of TEMPO were added to 5 mL of CH_3CN in a 10 mL Pyrex vessel. For the oxidation of secondary amines, 0.2 mmol of

secondary amines and 0.006 mmol of TEMPO were added to the reaction vessel. Then the reaction mixture was stirred for 30 min in dark to reach adsorption equilibrium. The 10 mL reaction Pyrex vessel was capped with butyl rubber septum. Then a rubber hole puncher was used to punch a hole in the rubber septum to connect with air to supply the oxygen demand in the experimental process. The reaction mixture was magnetically stirred at 1500 rpm and illuminated with blue LEDs in an air-conditioned room with additional electronic fan cooling to warrant the reaction temperature constantly at 25 °C. At the end of reaction, the ARS- TiO_2 particles were separated from the reaction mixture by centrifugation and the products were quantitatively analyzed by gas chromatography (GC) equipped with a flame ionization detector (FID) using chlorobenzene as the internal standard. The structures of products were confirmed by comparison with the retention time with authentic samples and further confirmed by gas chromatography–mass spectrometry (GC-MS).

2.4. General instrumentation and conditions

The gas chromatography (GC) quantitative measurements of conversions of substrates and selectivities of products were made on a gas chromatograph (Agilent 7890B) equipped with a flame ionization detector (FID) using high pure N_2 as the carrier gas and an Agilent J & W DB-5 capillary column (30 m \times 0.32 mm \times 0.25 μ m, 19091J-413) in the case of entries 1–13 of Table 4 and entries 1–4, 8, 12–14 of Table 5.

For some substrates in Table 5 including entries 5–7, 9–11, an Agilent J & W DB-17 capillary column (30 m \times 0.32 mm \times 0.25 μ m, 123–1732) was used for the quantitatively analysis of the products.

GC-FID standard analysis conditions: injector temperature 250 °C, detector temperature 280 °C, column temperature program: 50 °C (hold 1 min) raised up to 280 °C (hold 2 min) at a rate of 20 °C/min. The results were all obtained using a split mode with a split ratio is 30:1. For Table 4, entry 13, the sample was diluted to 1/10 with CH_3CN before analysis by GC-FID. For Table 5, entries 5–7, 9–11, column temperature program: 50 °C (hold 1 min) raised up to 280 °C (hold 2 min) at a rate of 10 °C/min.

Gas chromatography–mass spectrometry (GC-MS) analysis was performed on a Shimadzu GC 2010 gas chromatograph equipped with a Shimadzu GCMS-QP2010 Ultra electron ionization mass spectrometer using a Restek (Rxi[®]-5Sil MS) capillary column (30 m \times 0.25 mm \times 0.25 μ m) with high pure He as the carrier gas.

Table 1

Control experiments for the photocatalytic selective oxidation of benzylamine to imine under visible light irradiation^[a].

$2 \text{ Ph-NH}_2 \xrightarrow{\text{reaction conditions}} \text{Ph-N=Ph}$			
Entry	Conditions	Conv. [%] ^[b]	Sel. [%] ^[b]
1	Standard	76	97
2	Dark	0	0
3	No TEMPO	41	88
4	TiO_2	17	95
5	TiO_2 , TEMPO	15	80
6	TEMPO	0	0
7	ARS, TEMPO	8	99
8	ARS	9	99
9	N_2	2	62
10	Air (0.1 MPa)	96	96
11	O_2 (0.1 MPa)	100	93
12	blank	0	0
13 ^[c]	BQ (0.2 equiv.)	10	97
14	$AgNO_3$ (1 equiv.)	31	62

[a] Reaction conditions: 0.3 mmol of benzylamine, 10.7 mg of ARS- TiO_2 (0.002 mmol of ARS), 0.009 mmol of TEMPO, 5 mL of CH_3CN , 1 atm of air, 3 W blue LED irradiation, 2 h.

[b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine. [c] BQ, *para*-benzoquinone.

Table 2

The influence different dye and metal oxide on the photocatalytic selective oxidation of benzylamine to imine under visible light irradiation^[a].

Entry	Conditions	Conv. [%] ^[b]	Sel. [%] ^[b]
1	ARS-TiO ₂	14	98
2	NFR-TiO ₂	27	98
3	ARS-TiO ₂	76	97
4	ARS-ZnO	3	97
5	ARS-SiO ₂	3	97
6	ARS-γ-Al ₂ O ₃	2	97

[a] Reaction conditions: 0.3 mmol of benzylamine, organic dye-metal oxide (0.002 mmol of organic dye; 0.125 mmol of metal oxide), 0.009 mmol of TEMPO, 5 mL of CH₃CN, 1 atm of air, 3 W blue LED irradiation, 2 h. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

Table 3

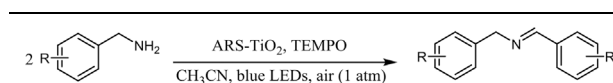
The influence of the amount of TEMPO on the selective aerobic oxidation of benzylamine to imine with O₂ by ARS-TiO₂^[a].

Entry	TEMPO [μmol]	Conv. [%] ^[b]	Sel. [%] ^[b]
1	0	41	88
2	3	62	94
3	6	71	95
4	9	76	97
5	12	80	97
6	15	88	97
7	18	86	97
8	21	87	97
9	24	89	98
10	27	93	99
11	30	91	98

[a] Reaction conditions: 0.3 mmol of benzylamine, 10.7 mg of ARS-TiO₂ (0.002 mmol of ARS), 5 mL of CH₃CN, 3 W blue LED irradiation, 1 atm of air, 2 h. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

Table 4

Visible light photocatalytic selective oxidation of primary amines to imines with O₂ by ARS-TiO₂ and TEMPO^[a].



Entry	Substrate	Product	T[h]	Conv. [%] ^[b]	Sel. [%] ^[b]
1			2.7	96	92
2			2.5	95	94
3			3.5	90	94
4			3.5	91	95
5			2.5	97	92
6			2.0	98	97
7			3.0	96	95
8			3.0	93	95
9			3.3	91	95
10			3.5	82	85
11			1.5	87	80
12			1.5	57	90
13 ^[c]			24	80	93

[a] Reaction conditions: 0.3 mmol of primary amine, 10.7 mg of ARS-TiO₂ (0.002 mmol of ARS), 0.009 mmol of TEMPO, 5 mL of CH₃CN, 3 W blue LED irradiation, 1 atm of air. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of amine, selectivity of corresponding imine. [c] 3 mmol of benzylamine, 0.03 mmol of TEMPO.

Table 5

Visible light photocatalytic selective oxidation of secondary amines to imines with O₂ by ARS-TiO₂ and TEMPO^[a].

Entry	Substrate	Product	T[h]	Conv. [%] ^[b]	Sel. [%] ^[b]
1			3.5	82	84
2			3.0	83	83
3			3.5	87	85
4			3.5	84	87
5			3.5	57	67
6			3.5	54	61
7			3.5	49	61
8			5.0	88	92
9			5.0	99	94
10			5.5	80	91
11			4.5	93	90
12			5.0	82	96
13			5.0	83	94
14			3.0	83	69

[a] Reaction conditions: 0.2 mmol of secondary amine, 10.7 mg of ARS-TiO₂ (0.002 mmol of ARS), 0.006 mmol of TEMPO, 5 mL of CH₃CN, 3 W blue LED irradiation, 1 atm of air. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of amine, selectivity of corresponding imine.

2.5. Light source

The light-emitting diodes (LEDs) were supplied by Shenzhen Qilai Optoelectronics Science and Technology Co., LTD., China. The reaction was usually irradiated with blue LEDs. In detail, four LED lamps were fastened around a magnetic stirrer in a circle in which the light irradiation was centered on the 10 mL Pyrex vessel. For blue LEDs, the irradiating wavelength range is 460 ± 10 nm with the irradiation peak around 460 nm. Thus, the possible heating of the reaction medium by infrared light and possible leaking of UV light are completely excluded.

3. Results and discussion

Visible-light-induced selective aerobic oxidation of benzylamine to *N*-benzylidenbenzylamine was selected as the probe reaction. Table 1 summarizes the detailed control experiments for the aerobic oxidation of amine to imines. Under standard reaction conditions of ARS-TiO₂ coupled with TEMPO, the selective oxidation of benzylamine to imine with O₂ in ambient air could be achieved under visible light irradiation (entry 1, Table 1). Without visible light irradiation, the reaction could not proceed (entry 2, Table 1), suggesting that it is a photocatalytic reaction. Without TEMPO, both the conversion and the selectivity were significantly lowered (entry 3, Table 1), as indicated in Scheme 1. The selective aerobic oxidation of amines occurred to some degree on the surface of TiO₂ (entries 4 and 5, Table 1). This is attributed to a visible-light-absorbing surface complex being formed by the interaction of benzylamine and TiO₂, as previously reported [23].

Without TiO₂, the reaction totally stopped or became very sluggish (entries 6–8, Table 1), demonstrating the pivotal role of TiO₂ in the activation of O₂, in line with the proposed mechanism in Scheme 1. Without O₂, the reaction almost stopped (entry 9, Table 1); the reaction rates improved with an increased partial pressure of O₂ (entries 10 and 11, Table 1), indicating that the oxidant of the reaction is O₂, agreeing well with Scheme 1. Without any of the photocatalytic components, the reaction did not occur at all (entry 12, Table 1). When 0.2 equivalents of the O₂^{•−} quencher *para*-benzoquinone (BQ) were added to the reaction system, the reaction rate was significantly reduced (entry 13, Table 1). As indicated in Scheme 1, O₂^{•−} was essential in the regeneration of TEMPO from TEMPOH. Thus, the ROS from the conduction band of TiO₂ was effectively used in the catalytic cycle, conferring a high selectivity for imine. Furthermore, when 1 equiv. of AgNO₃ was added to the system as an electron acceptor competitor to O₂, both the conversion for benzylamine and the selectivity for imine were significantly dropped (entry 14, Table 1) which is attributed to the partial shutdown of the generation of O₂^{•−} by Ag⁺ accepting e_{cb}[−] rather than O₂.

The industrial synthesis of H₂O₂ from H₂ and O₂ was based on an anthraquinone process [24], which is indicative of the robustness of anthraquinone framework under oxidative conditions. Therefore, we selected several organic dyes with anthraquinone motif within the molecular structure to carry out the visible-light-induced selective aerobic oxidation of amines (entries 1–3, Table 2). Three dyes (see Fig. 1) such as alizarin blue S (ABS), nuclear fast red (NFR) and ARS were tested as sensitizers for TiO₂ in which ARS gives the best activity (entry 3, Table 2). If TiO₂ was replaced by redox-inactive oxides (entries 4–6, Table 2), the reaction ceased, further affirming the critical

redox role of TiO₂. Thus, ARS-TiO₂ is the most active photocatalyst for the selective photocatalytic oxidation of benzylamine. Moreover, the state of ARS on TiO₂ (see ARS-TiO₂, Fig. 1) and its photochemical behavior has been well established by others [25–27] that could be very helpful for one to understand the unique activity of ARS-TiO₂. The diffuse reflectance UV–vis spectra of ARS, TiO₂ and ARS-TiO₂ were shown in Fig. S1.

Next, the influence of TEMPO on the visible-light-induced selective aerobic oxidation of benzylamine to imine by ARS-TiO₂ was thoroughly investigated. The results are shown in Table 3. Without TEMPO, the oxidation of benzylamine proceeded with a low reaction rate and imine selectivity (entry 1, Table 3). If catalytic amounts of TEMPO were added to the reaction system, the reaction results were much improved in terms of both reaction rate and product selectivity (entries 2–11, Table 3). These results suggest that TEMPO plays a pivotal role in the electron relay process leading to the completion of the cooperative photocatalysis. At the initial stage, the conversion rates improved with increasing amounts of TEMPO (entries 2–6, Table 3). Nevertheless, this promising effect plateaus with further increases (entries 7–11, Table 3), hinting that there might be a saturation point for the potential of TEMPO in mediating the electron flows for a system of cooperative photocatalysis.

As shown in Scheme 1, both ARS and TEMPO are redox-active organic molecules that can undergo reversible redox recycling in CH₃CN under visible light irradiation. After establishing this pattern, the reaction mechanism was further investigated with kinetic studies to follow the conversion of benzylamine, the change of TEMPO and the formation of imine. Fig. 2 illustrates the interplay of these factors. The conversion of benzylamine fit almost linearly with time, indicative of the reaction following zero-order kinetics. This is a rare phenomenon, as most heterogeneous catalytic reactions obey pseudo-first-order kinetics. The high selectivity for imine was maintained throughout the reaction process. When the conversion of benzylamine was low, TEMPO was almost unchanged. With the progress of time, TEMPO was lost to some extent. However, 84% of TEMPO remained at the end of the reaction.

The reaction kinetics constant k_H for the oxidation of benzylamine is $0.0607 \text{ mol L}^{-1} \text{ h}^{-1}$ under the stated reaction conditions (Fig. S2). To more deeply understand the mechanism, the reaction kinetic isotope effect (KIE) was investigated. Thus, the C_α-H hydrogen atom of benzylamine was replaced by deuterium (C_α-D) and subjected to the same kinetics studies. The reaction kinetics constant k_D for the oxidation of benzyl- α , α -d₂-amine is $0.0363 \text{ mol L}^{-1} \text{ h}^{-1}$ (Fig. S3). The KIE value was determined to be 1.67 ± 0.2 . This value indicates that it belongs to primary KIE. However, the value of this range cannot suggest that the cleavage of C_α-H during the activation of benzylamine is the rate-determining step of the overall process. But the photocatalytic cleavage of C_α-H of benzylamine plays an important role in altering the reaction rate. This agrees well with Scheme 1, in which the abstraction of hydrogen in amines by TEMPO⁺ to TEMPOH is the key step.

The influence of different amounts of the solvent, CH₃CN, is shown in Table S1, revealing an almost negligible impact. According to zero-order kinetics, this result should be expected. One might doubt that the irradiation areas of the reaction in a Pyrex vial could be influenced by the different amounts of CH₃CN, therefore leading to different results. It should be noted that the reaction medium was stirred rapidly

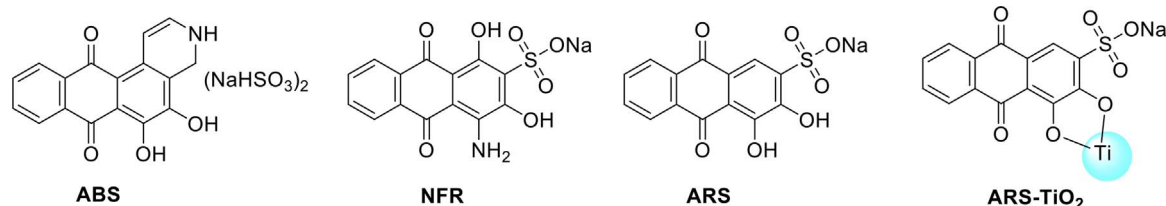


Fig. 1. The molecular structures of anthraquinone dyes used as sensitizers and the adsorption mode of ARS-TiO₂.

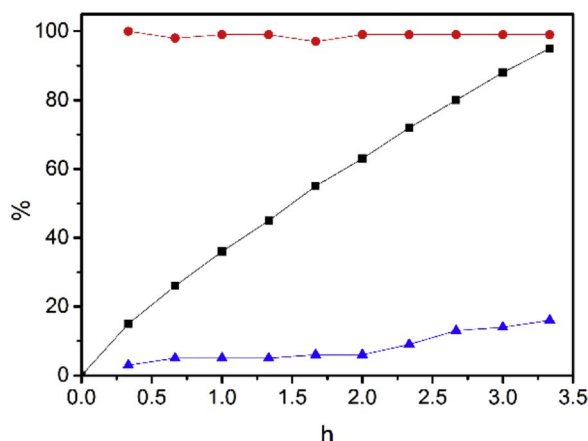


Fig. 2. Reaction kinetics plot for the visible light photocatalytic oxidation of benzylamine to imine with air by ARS-TiO₂ and TEMPO. Reaction conditions: 0.3 mmol of benzylamine, 0.009 mmol of TEMPO, 10.7 mg of ARS-TiO₂, 1.5 mL of CH₃CN, 3 W blue LED irradiation, 1 atm of air. Red circle, selectivity of *N*-benzylidenebenzylamine; black square, conversion of benzylamine; blue triangle, change of TEMPO. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(1500 rpm) throughout the experiment, which could minimize the difference in irradiation area.

With the mechanistic insights in hand, we next investigated the substrate scope for this reaction protocol. The results for the oxidative coupling of primary amine and its derivatives to their corresponding imines are summarized in Table 3. With the surface of anatase TiO₂ as the reaction platform, the oxidative coupling of various primary benzyl amines to the corresponding imines in the presence of 0.667 mol% ARS and 3 mol% TEMPO under visible light irradiation occurred rapidly and with high selectivity (entries 1–10, Table 4). These results are much better in terms of both selectivity and efficiency than those of the photocatalytic selective oxidation of amines with TiO₂ under UV irradiation with a 100 W of Hg lamp or visible light irradiation with a 300 W Xe lamp [23,28].

A wide arrange of benzylamines with electron-withdrawing or electron-donating substituted groups can be tolerated under the standard conditions to obtain the desired product. There are only slight differences in reaction time for *para*-substituted benzylamines (entries 2 and 5–9, Table 4). Notably, benzylamines with electron-donating groups require less time than benzylamine (entries 2, 5, and 6 vs. entry 1, Table 4). In contrast, more time is required for benzylamines with electron-withdrawing groups (entries 7–9 vs. entry 1, Table 4). To deepen the understanding of the impact of electronic effect of the substituted groups, we carried out kinetic studies on the oxidation of Me, H- and Br- substituted benzyl amines (Fig. S4). The rate constants of k_{Me} , k_{H} and k_{Br} are 0.0351 mol L⁻¹ h⁻¹, 0.0287 mol L⁻¹ h⁻¹ and 0.0229 mol L⁻¹ h⁻¹ in an order of $k_{\text{Me}} > k_{\text{H}} > k_{\text{Br}}$. Benzylamine with a methoxy group at the *meta*- or *ortho*- position requires more time to achieve conversions comparable to that of *para*-substituted benzylamine (entries 3 and 4 vs. entry 2, Table 4). A di-substituted group such as 3,4-methylenedioxy also requires more time with lower selectivity (entry 10, Table 4). Amines with heteroatom-containing aromatic rings could achieve good results. (entries 11 and 12, Table 4).

In addition, the reusability of ARS-TiO₂ was carried out. At 50% conversion of benzylamine, the ARS-TiO₂ photocatalyst can be recycled three times with only slight loss of photocatalytic activity (from 50% to 41% conversion). The diffuse reflectance UV-vis and FT-IR spectra of ARS-TiO₂ before and after reaction are shown in Figs. S5. In addition, XRD characterization of the samples was also carried out (Fig. S6). These results evidence that TiO₂ is stable during the reaction; but there is degradation of ARS occurrence to some extent. To further demonstrate the redox recycling of the organic dye of ARS and TEMPO, we increased

the amount of benzylamine and decreased the molar ratio of TEMPO. A turnover number of 1200 in terms of ARS dye could be obtained in the presence of 1 mol% of TEMPO (entry 13, Table 4). This is one of the best results to date amongst the reported systems.

The visible light photocatalytic selective oxidation of secondary amines to imines is even more challenging. Therefore, in most reported cases, either primary or secondary amines can be subjected to the same conditions with high selectivity [28–30]. We have concluded that the formation of imine was due to the abstraction of C_α-H by TEMPO⁺ to yield the final product. One would expect this protocol to be applicable to the selective oxidation of secondary amines to their corresponding imines with air under visible light irradiation. Indeed, we found that the visible-light-induced selective aerobic oxidation of a variety of secondary amines could proceed smoothly under the photocatalytic reaction conditions (Table 5). Dibenzyl amine and its derivatives could be successfully oxidized to their corresponding imines with 1 atm of air in the presence of 1 mol% of ARS and 3 mol% of TEMPO under visible light irradiation on the surface of anatase TiO₂ (entries 1–7, Table 5). For the synthesis of given target molecules, intramolecular reactions are typically much faster than intermolecular reactions [31]. However, the results here do not follow this rule in which the oxidation rates of dibenzyl amines are much slower than that of primary benzylamines (entries 1–7, Table 5 vs. entries 1–8, Table 4). This might be attributed to the steric hindrance during the interaction between TEMPO⁺ and secondary benzyl amines, which in turn leads to slower reaction rates and relatively lower selectivity towards imines. *N*-*tert*-Butyl benzylamine and its substituted derivatives can withstand the reaction conditions to deliver high imine selectivity, although they require longer times (entries 8–13, Table 5). For *N*-isopropyl benzylamine, with the C_α-H presence at the non-benzyl side, the selectivity is comparatively low (entry 14, Table 5).

In summary, we have developed a highly efficient protocol for the visible-light-induced selective oxidation of both primary and secondary amines to their corresponding imines with ambient air by dye-sensitized TiO₂ and TEMPO. Akin to natural photosynthesis, each individual component is explored for its best potential. And the intricate synergy of TiO₂, organic dyes, TEMPO and O₂ gives rise to the unprecedented general protocol. Importantly, this discovery could pave the way for more exciting oxidation reactions under visible light irradiation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.10.002>.

References

- [1] X.J. Lang, W.H. Ma, C.C. Chen, H.W. Ji, J.C. Zhao, Acc. Chem. Res. 47 (2014) 355–363.
- [2] F. Parrino, G. Camera Roda, V. Loddo, L. Palmisano, Angew. Chem. Int. Ed. 55 (2016) 10391–10395.
- [3] A. Fujishima, K. Honda, Nature 238 (1972) 37–38.
- [4] C.M. Friend, Chem. Rec. 14 (2014) 944–951.
- [5] C.J. Li, G.R. Xu, B.H. Zhang, J.R. Gong, Appl. Catal., B 115 (2012) 201–208.
- [6] T. Kamegawa, S. Matsuura, H. Seto, H. Yamashita, Angew. Chem. Int. Ed. 52 (2013) 916–919.
- [7] D. Mitoraj, H. Kisch, Angew. Chem. Int. Ed. 47 (2008) 9975–9978.
- [8] S. Sakthivel, H. Kisch, Angew. Chem. Int. Ed. 42 (2003) 4908–4911.
- [9] D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, Chem. Soc. Rev. 38 (2009) 1999–2011.
- [10] L. Özcan, S. Yurdakal, V. Augugliaro, V. Loddo, S. Palmas, G. Palmisano, L. Palmisano, Appl. Catal., B 132–133 (2013) 535–542.
- [11] M. Neumann, S. Fuldner, B. König, K. Zeitler, Angew. Chem. Int. Ed. 50 (2011)

- 951–954.
- [12] T.P. Yoon, M.A. Ischay, J. Du, *Nat. Chem.* 2 (2010) 527–532.
- [13] D. Ravelli, M. Fagnoni, A. Albini, *Chem. Soc. Rev.* 42 (2013) 97–113.
- [14] T. Kamegawa, H. Seto, S. Matsuura, H. Yamashita, *ACS Appl. Mater. Interfaces* 4 (2012) 6635–6639.
- [15] X.J. Lang, X.D. Chen, J.C. Zhao, *Chem. Soc. Rev.* 43 (2014) 473–486.
- [16] J.H. Kou, C.H. Lu, J. Wang, Y.K. Chen, Z.Z. Xu, R.S. Varma, *Chem. Rev.* 117 (2017) 1445–1514.
- [17] Y. Nosaka, A.Y. Nosaka, *Chem. Rev.* 117 (2017) 11302–11336.
- [18] X.J. Lang, J.C. Zhao, X.D. Chen, *Chem. Soc. Rev.* 45 (2016) 3026–3038.
- [19] M. Largeron, M.B. Fleury, *Science* 339 (2013) 43–44.
- [20] M. Largeron, M.B. Fleury, *Angew. Chem. Int. Ed.* 51 (2012) 5409–5412.
- [21] X.J. Lang, J.C. Zhao, X.D. Chen, *Angew. Chem. Int. Ed.* 55 (2016) 4697–4700.
- [22] A. Badalyan, S.S. Stahl, *Nature* 535 (2016) 406–410.
- [23] X.J. Lang, W.H. Ma, Y.B. Zhao, C.C. Chen, H.W. Ji, J.C. Zhao, *Chem. Eur. J.* 18 (2012) 2624–2631.
- [24] J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, *Angew. Chem. Int. Ed.* 45 (2006) 6962–6984.
- [25] Y. Di Iorio, E.S. Román, M.I. Litter, M.A. Grela, *J. Phys. Chem. C* 112 (2008) 16532–16538.
- [26] W. Ji, Y. Wang, I. Tanabe, X.X. Han, B. Zhao, Y. Ozaki, *Chem. Sci.* 6 (2015) 342–348.
- [27] G.M. Liu, X.Z. Li, J.C. Zhao, S. Horikoshi, H. Hidaka, *J. Mol. Catal., A* 153 (2000) 221–229.
- [28] X.J. Lang, H.W. Ji, C.C. Chen, W.H. Ma, J.C. Zhao, *Angew. Chem. Int. Ed.* 50 (2011) 3934–3937.
- [29] Y.H. Wu, B. Yuan, M.R. Li, W.H. Zhang, Y. Liu, C. Li, *Chem. Sci.* 6 (2015) 1873–1878.
- [30] Z.J. Wang, S. Ghasimi, K. Landfester, K.A.I. Zhang, *Adv. Mater.* 27 (2015) 6265–6270.
- [31] E.V. Anslyn, D.A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, 2006, pp. 489–536.